

Pseudopotential theory for self-diffusion and impurity diffusion: Defect-energy calculations for fcc metals

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Generalized formulations for the calculation of energies of multivacancy formation and migration in pure and impure lattices and a multi-interstitial formation in otherwise pure lattices have been obtained with use of a pseudopotential scheme. The energies caused by relaxations of the surrounding neighbors are incorporated in these processes. Formulas relating self-diffusion and impurity diffusion via a vacancy mechanism have been discussed. Calculations of the vacancy-formation energy, the migration energy, and hence the activation energy for self-diffusion and impurity diffusion and their changes have been done with use of standard model potentials. My calculations show that the effect of relaxations of the surrounding neighbors of the migrating atom at its activated position is significant while it has negligible effect in vacancy-formation process. The calculations also show that a Heine-Abarenkov model explains successfully all the defect parameters but the Aschroft model does not. A more sophisticated multiparameter model or the Heine-Abarenkov two-parameter model with approximate explanation of all the atomic properties is perhaps a better choice. It is also noted that careful numerical computation is essential for achieving satisfactory agreement with experiment.

I. INTRODUCTION

In the pseudopotential theory of Harrison,¹ a second-order perturbation technique was used. There the structure-dependent electrostatic and band-structure energies were calculated. The former depends on the ion-ion interaction while, the latter is derived from the interaction of ion-electron and electron-electron by a proper choice of the pseudopotential, dielectric function, and exchange and correlation. These energies are also dependent on the structure factor of a particular defected lattice and sometimes on the modified lattice wave numbers. The modification in the lattice wave number from its perfect lattice value is necessary for the maintenance of the constancy in the lattice volume and in the number of lattice ions.

Using this method, DuCharme and Weaver² successfully calculated the vacancy-formation and migration energies in different cubic metals. This method was also used for the calculation of vacancy-impurity binding energy by Yamamoto and co-workers^{3,4} and migration energy for monovacancy and divacancy considering relaxations of the surrounding neighbors at the saddle-point configuration by Takai, Doyama, and Hisamatsu.⁵ Recently this method has been successfully applied to the impurity diffusion of tin in lead by a vacancy mechanism.⁶ This method has also been successfully used to calculate the energetics of split and nonsplit interstitial formation energies in some fcc metals.⁷

Calculation of energetics of point defects like vacancy, interstitial, or substitutional impurity uses generally simple model potentials like Aschroft's empty-core model,⁸ Heine and Abarenkov's local and nonlocal models,^{6,9} Harrison's point-ion model,¹ Ziman model,¹⁰ etc. with a proper choice of the dielectric function, and exchange

and correlation; a review has been given by Cohen and Heine.⁹ Recently a more sophisticated resonant model potential has been developed in a semirelativistic manner by Dagens¹¹ and a molecular-dynamics code has been used to calculate the energetics of interstitials, vacancies, and substitutional impurities.¹² Here, however, in this paper this sophisticated potential has not been used, for the sake of simplicity, but a complete calculation of self-diffusion and impurity diffusion via a vacancy mechanism has been given with use of simple model potentials, viz., those of Aschroft and of Heine and Abarenkov. These models, however, are not above criticism as (i) they are very sensitive to changes in their parameters and (ii) they consider only *s-p* electrons but not *s-d* hybridization, which plays an important role in the calculation of energies in noble metals. So a real test of using these models will be in the construction of interatomic potentials and the application to explain different atomic properties. One such application to the lattice statics method¹³ was done by Singhal.¹⁴ Sen and Sarkar¹⁵ obtained fitted values of the parameters of Heine and Abarenkov's model from an approximate overall explanation of atomic properties.

Here generalized formulations for this purpose have been given for different types of defected lattices from which different defect energies can be calculated, viz., (i) vacancy-formation energy (E_{FH}^{1v}) and its change in presence of impurity at an adjacent site, i.e., vacancy-impurity binding (ΔE_F), (ii) vacancy-migration energy (E_{MH}^{1v}) and its change for vacancy-impurity atom exchange (ΔE_M), (iii) activation energy (Q_0) and its differential change (ΔQ), and (iv) interstitial formation energy (E_{FH}^{1i}) in an otherwise pure lattice. Finally, in the section on results and discussions, calculations of defect energies necessary for self-diffusion and impurity diffusion via a vacancy mechanism have been dealt with.

II. PURE LATTICE

In a pure lattice the total structure-dependent energy is given by¹⁶

$$E^P = \sum'_q |S(q)|^2 U(q) - \lim_{\eta \rightarrow \infty} Z_H^2 e^2 (\eta/\pi)^{1/2}, \quad (1)$$

where

$$U(q) = \lim_{\eta \rightarrow \infty} (2\pi Z_H^2 e^2 / \Omega_H q^2) \exp(-q^2/4\eta) + [\omega_H(q)]^2 \epsilon_H(q) \chi_H(q), \quad (1a)$$

the subscript H is for host, Z_H the valency of the host, Ω_H the atomic volume, e the electronic charge, η the convergence factor, $\omega_H(q)$ the pseudopotential, $\epsilon_H(q)$ the dielectric function, $\chi_H(q)$ the perturbation characteristics, and q_0 the lattice wave number. The first term of Eq. (1a) is the electrostatic energy and the second term is

the band-structure energy. The structure factor $S(q)$ for a perfect lattice can be defined as

$$S(q) = \begin{cases} 1 & \text{for } \mathbf{q} = \mathbf{q}_0 \\ 0 & \text{for } \mathbf{q} \neq \mathbf{q}_0 \end{cases}. \quad (2)$$

Now any defect formation or migration energy can be defined as the difference of the total structural energy for the whole lattice after and before the defect is created, i.e.

$$E_{\text{defect}} = N(E_{\text{after}} - E_{\text{before}}), \quad (3)$$

where N is the total number of lattice ions. From Eq. (3) expressions for different defect energies can be derived.

III. LATTICE WITH IMPURITIES AND VACANCIES

Let us now consider a lattice containing v vacancies and I impurities with a total of N ions ($v, I \ll N$). The total structure-dependent energy (E^{Iv}) in this case will be

$$E^{Iv} = \sum'_q \left[|S_v(q)|^2 U(q) + \sum_{i=1}^I \{ \exp[i\mathbf{q} \cdot \mathbf{r}_i] S_v(q) + \exp[-i\mathbf{q} \cdot \mathbf{r}_i] S_v^*(q) \} \Delta U(q) + \sum_{i=1}^I \sum_{j=1}^I \exp(i\mathbf{q} \cdot [\mathbf{r}_i - \mathbf{r}_j]) \Delta^2 U(q) \right] - \left[1 + \frac{I}{N} \left(\frac{Z_I^2}{Z_H^2} - 1 \right) \right] \lim_{\eta \rightarrow \infty} 2Z_H^2 e^2 (\eta/\pi)^{1/2}, \quad (4)$$

where

$$S_v(q) = \left[\sum_{i=1}^{N+v} \exp(-i\mathbf{q} \cdot \mathbf{r}_i) - \sum_{i=1}^v \exp(-i\mathbf{q} \cdot \mathbf{r}_i) \right] / N, \quad (4a)$$

$$\Delta U(q) = \lim_{\eta \rightarrow \infty} [2\pi Z_H (Z_I - Z_H) e^2 / \Omega_H q^2] \exp(-q^2/4\eta) + [\omega_I(q) - \omega_H(q)] \omega_H(q) \epsilon_H(q) \chi_H(q), \quad (4b)$$

and

$$\Delta^2 U(q) = \lim_{\eta \rightarrow \infty} [2\pi (Z_I - Z_H)^2 e^2 / \Omega_H q^2] \exp(-q^2/4\eta) + [\omega_I(q) - \omega_H(q)]^2 \epsilon_H(q) \chi_H(q). \quad (4c)$$

The subscript I is for impurity, Z_I the impurity valency, $\omega_I(q)$ the corresponding pseudopotential, and \mathbf{r}_i and \mathbf{r}_j the position vectors for the i th and j th lattice sites, respectively. The replacement of $S_v(q)$ by $S(q)$ gives us the expression for structure-dependent energy of a lattice with I number of impurities (E^I).

The number of lattice sites in this case of lattice with impurities and vacancies is increased to $N+v$ and so the lattice wave numbers will be scaled up to μq_0 with $\mu = 1 + v/3N$ to maintain the constancy in the volume. Hence the v -vacancy-formation energy in the presence of I impurities may be given as

$$E_{fI}^{vv} = N(E^{Iv} - E^I) = \sum_{q_0} \frac{v q_0}{3} \frac{\partial U(q_0)}{\partial q_0} + \frac{\Omega_H}{2\pi^2} \int_0^\infty \sum_{i=1}^v \sum_{j=1}^v \alpha_{ij}(q) U(q) q^2 dq - \frac{\Omega_H}{\pi^2} \int_0^\infty \sum_{i=1}^v \sum_{j=1}^I \alpha_{ij}(q) \Delta U(q) q^2 dq. \quad (5)$$

The expression for monovacancy-formation energy^{1,2} (E_{fH}^{1v}) can be obtained by putting $v=1$ and $I=0$ in Eq. (5). Similarly when $v=I=1$, one gets the monovacancy-formation energy in presence of an impurity at an adjacent site (E_{fI}^{1v}) and the vacancy-impurity binding energy (ΔE_f) from the difference ($\Delta E_f = E_{fI}^{1v} - E_{fH}^{1v}$).^{3,16} In the same manner one gets the expressions for divacancy-formation energy (E_{fH}^{2v}) and divacancy-binding energy ($E_b^{2v} = E_{fH}^{2v} - 2E_{fH}^{1v}$).

But to obtain exact expressions for the vacancy-formation energy and vacancy-impurity binding energy, knowledge of the contribution to the energy caused by the relaxation of neighbors around a vacancy in the process of vacancy formation is essential. Though this contribution may be small, as pointed out by Yamamoto *et al.*,¹⁷ still for an exact and complete representation the formulation for the relaxation part of v -vacancy-formation in the presence of I impurities has been done

here. Let the number of relaxed neighbors around a vacancy be n and the position vector for the j th neighbor around the i th vacancy be \mathbf{r}_{ij} whose relaxed position is \mathbf{r}'_{ij} . The structure factor and the relaxation energy in this process are given by

$$S_{vR}(q) = \left[\sum_{i=1}^{N+v} \exp(-i\mathbf{q}\cdot\mathbf{r}_i) - \sum_{i=1}^v \exp(-i\mathbf{q}\cdot\mathbf{r}_i) + \sum_{i=1}^v \sum_{j=1}^n \{ \exp(-i\mathbf{q}\cdot\mathbf{r}'_{ij}) - \exp(-i\mathbf{q}\cdot\mathbf{r}_{ij}) \} \right] / N, \quad (6)$$

and

$$E_{fRI}^{vv} = \sum'_{q_0} \sum_{i=1}^v \sum_{j=1}^n 2[\cos(\mathbf{q}_0\cdot\mathbf{r}'_{ij}) - \cos(\mathbf{q}_0\cdot\mathbf{r}_{ij})]U(q_0) + \frac{\Omega_H}{2\pi^2} \int_0^\infty [a_1(q)U(q) + 2a_2(q)\Delta U(q)]q^2 dq, \quad (7)$$

where

$$a_1(q) = \sum_{i=1}^v \sum_{j=1}^v \sum_{k=1}^n [\beta_{ijk}(q) - \beta'_{ijk}(q)] + \sum_{i=1}^v \sum_{j=1}^n \sum_{k=1}^v \sum_{l=1}^n [\gamma_{ijkl}(q) - 2\gamma'_{ijkl}(q) + \gamma''_{ijkl}(q)], \quad (7a)$$

and

$$a_2(q) = \sum_{i=1}^I \sum_{j=1}^v \sum_{k=1}^n [\beta'_{ijk}(q) - \beta_{ijk}(q)]. \quad (7b)$$

$\alpha_{ij}(q)$, $\beta_{ijk}(q)$, $\beta'_{ijk}(q)$, $\gamma_{ijkl}(q)$, $\gamma'_{ijkl}(q)$, and $\gamma''_{ijkl}(q)$ are defined in Sec. V. Hence the total monovacancy-formation energy is $E_{FH}^{1v} = E_{fH}^{1v} + E_{fRH}^{1v}$ and the vacancy-impurity binding energy is $\Delta E_F = \Delta E_f + \Delta E_{fR}$ where $\Delta E_{fR} = E_{fRI}^{1v} - E_{fRH}^{1v}$, which can be obtained from Eqs. (5) and (7).

IV. MIGRATION OF HOST AND IMPURITY IN AN IMPURE LATTICE

This section deals with another dilute binary alloy system in which there are v vacancies, m host migrating atoms, and p solute migrating atoms out of a total number of I impurities (clearly $m+p < v$ and $I \ll N$). Let the saddle-point configuration of any i th migrating atom be \mathbf{r}_{a_i} . The structure factor and the migration energy for m hosts and p impurities are given by

$$S_m(q) = S_v(q) + \frac{1}{N} \sum_{i=1}^m [\exp(-i\mathbf{q}\cdot\mathbf{r}_{a_i}) - \exp(-i\mathbf{q}\cdot\mathbf{r}_i)] + \frac{1}{N} \sum_{i=1}^p [\exp(-i\mathbf{q}\cdot\mathbf{r}_{a_i}) - \exp(-i\mathbf{q}\cdot\mathbf{r}_i)] \quad (8)$$

and

$$E_{mI}^{mpv} = \sum'_{q_0} \left[\sum_{i=1}^{m+p} 2(\cos\mathbf{q}_0\cdot\mathbf{r}_{a_i} - 1)U(q_0) + \sum_{i=1}^p 2(\cos\mathbf{q}_0\cdot\mathbf{r}_{a_i} - 1)\Delta U(q_0) \right] + (\Omega_H/2\pi^2) \int_0^\infty [A_1(q)U(q) + A_2(q)\Delta U(q) + A_3(q)\Delta^2 U(q)]q^2 dq, \quad (9)$$

where

$$A_1(q) = 2 \left[\sum_{i=1}^v \sum_{j=1}^m + \sum_{i=1}^v \sum_{j=1}^p \right] [\alpha_{ij}(q) - \delta_{ij}(q)] + \left[\sum_{i=1}^m \sum_{j=1}^m + 2 \sum_{i=1}^m \sum_{j=1}^p + \sum_{i=1}^p \sum_{j=1}^p \right] \times [\alpha_{ij}(q) - 2\delta_{ij}(q) + \theta_{ij}(q)], \quad (9a)$$

$$A_2(q) = 2 \left[\sum_{i=1}^v \sum_{j=1}^p - \sum_{i=1}^I \sum_{j=1}^m - \sum_{i=1}^I \sum_{j=1}^p \right] [\alpha_{ij}(q) - \delta_{ij}(q)] + \left[\sum_{i=1}^m \sum_{j=1}^p + \sum_{i=1}^p \sum_{j=1}^p \right] [\alpha_{ij}(q) - 2\delta_{ij}(q) + \theta_{ij}(q)], \quad (9b)$$

and

$$A_3(q) = \sum_{i=1}^p \sum_{j=1}^p [\alpha_{ij}(q) - 2\delta_{ij}(q) + \theta_{ij}(q)] - 2 \sum_{i=1}^I \sum_{j=1}^p [\alpha_{ij}(q) - \delta_{ij}(q)]. \quad (9c)$$

$\delta_{ij}(q)$ and $\theta_{ij}(q)$ are defined in Sec. V. The expressions for the monovacancy-migration energy (E_{mH}^{1v}),² the monovacancy-migration energy in the presence of impurity at the near-neighbor position of the vacancy (E_{mI}^{1v}),^{6,16} and hence their change ($\Delta E_m = E_{mI}^{1v} - E_{mH}^{1v}$),^{6,16} can be obtained by putting, respectively, $v = m = 1$ and $I = p = 0$ and $v = m = I = p = 1$. Similarly, one can obtain the other expressions.

In this process of migration when a migrating atom is at the activated position the surrounding neighbors around it will relax to accommodate the migrating atom at the position. So the total migration energy will also contain a term corresponding to relaxation energy, which is calculated as

$$E_{mRI}^{mpv} = \sum'_{q_0} \sum_{i=1}^{m+p} \sum_{j=1}^k 2[\cos(\mathbf{q}_0\cdot\mathbf{r}'_{ij}) - \cos(\mathbf{q}_0\cdot\mathbf{r}_{ij})]U(q_0) + \frac{\Omega_H}{2\pi^2} \int_0^\infty [b_1(q)U(q) + b_2(q)\Delta U(q)]q^2 dq, \quad (10)$$

where

$$\begin{aligned}
b_1(q) = & 2 \left[\sum_{i=1}^v \sum_{j=1}^m \sum_{k=1}^k + \sum_{i=1}^v \sum_{j=1}^p \sum_{k=1}^k \right] [\beta_{ijk}(q) - \beta'_{ijk}(q)] + 2 \left[\sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^k + \sum_{i=1}^m \sum_{j=1}^p \sum_{k=1}^k + \sum_{i=1}^p \sum_{j=1}^m \sum_{k=1}^k + \sum_{i=1}^p \sum_{j=1}^p \sum_{k=1}^k \right] \\
& \times [\beta_{ijk}(q) - \beta'_{ijk}(q) - \phi_{ijk}(q) + \phi'_{ijk}(q)] + \left[\sum_{i=1}^m \sum_{j=1}^k \sum_{k=1}^m \sum_{l=1}^k + \sum_{i=1}^m \sum_{j=1}^k \sum_{k=1}^p \sum_{l=1}^k + \sum_{i=1}^p \sum_{j=1}^k \sum_{k=1}^m \sum_{l=1}^k + \sum_{i=1}^p \sum_{j=1}^k \sum_{k=1}^p \sum_{l=1}^k \right] \\
& \times [\gamma_{ijkl}(q) - 2\gamma'_{ijkl}(q) + \gamma''_{ijkl}(q)] \quad (10a)
\end{aligned}$$

and

$$\begin{aligned}
b_2(q) = & 2 \left[\sum_{i=1}^I \sum_{j=1}^m \sum_{k=1}^k + \sum_{i=1}^I \sum_{j=1}^p \sum_{k=1}^k \right] [\beta'_{ijk}(q) - \beta_{ijk}(q)] \\
& + 2 \left[\sum_{i=1}^p \sum_{j=1}^m \sum_{k=1}^k + \sum_{i=1}^p \sum_{j=1}^p \sum_{k=1}^k \right] \\
& \times [\beta_{ijk}(q) - \beta'_{ijk}(q) - \phi_{ijk}(q) + \phi'_{ijk}(q)] . \quad (10b)
\end{aligned}$$

k is the number of relaxed neighbors and $\phi_{ijk}(q)$ and $\phi'_{ijk}(q)$ are defined in Sec. V. So the total migration energy for m host migrating atoms and p impurities is the sum total of E_{mI}^{mpv} and E_{mRI}^{mpv} , i.e., $E_{MI}^{mpv} = E_{mI}^{mpv} + E_{mRI}^{mpv}$, and hence exact values of the monovacancy-migration energy ($E_{MH}^{1v} = E_{mH}^{1v} + E_{mRH}^{1v}$) (Ref. 5) and its differential change ($\Delta E_M = \Delta E_m + \Delta E_{mR}$) (Refs. 6 and 16) can be calculated easily.

V. LATTICE WITH INTERSTITIALS

In this section another lattice containing t interstitials with the position vector for the i th interstitial being \mathbf{r}_{t_i} is considered. The number of lattice sites here is reduced to $N-t$ and to maintain the constancy in the volume the lattice wave numbers are modified to $\lambda \mathbf{q}_0$ with $\lambda = 1 - t/3N$. So the structure factor and the t -interstitial formation energy are

$$S_t(q) = \left[\sum_{i=1}^{N-t} \exp(-i\mathbf{q} \cdot \mathbf{r}_i) + \sum_{i=1}^t \exp(-i\mathbf{q} \cdot \mathbf{r}_{t_i}) \right] / N \quad (11)$$

$$\alpha_{ij}(q) = \sin(q|\mathbf{r}_i - \mathbf{r}_j|) / q|\mathbf{r}_i - \mathbf{r}_j|, \quad \delta_{ij}(q) = \sin(q|\mathbf{r}_i - \mathbf{r}_{a_j}|) / q|\mathbf{r}_i - \mathbf{r}_{a_j}|, \quad (14a)$$

$$\theta_{ij}(q) = \sin(q|\mathbf{r}_{a_i} - \mathbf{r}_{a_j}|) / q|\mathbf{r}_{a_i} - \mathbf{r}_{a_j}|, \quad \xi_{ij}(q) = \sin(q|\mathbf{r}_{t_i} - \mathbf{r}_{t_j}|) / q|\mathbf{r}_{t_i} - \mathbf{r}_{t_j}|, \quad (14b)$$

$$\beta_{ijk}(q) = \sin(q|\mathbf{r}_i - \mathbf{r}_{jk}|) / q|\mathbf{r}_i - \mathbf{r}_{jk}|, \quad \beta'_{ijk}(q) = \sin(q|\mathbf{r}_i - \mathbf{r}'_{jk}|) / q|\mathbf{r}_i - \mathbf{r}'_{jk}|, \quad (14c)$$

$$\phi_{ijk}(q) = \sin(q|\mathbf{r}_{a_i} - \mathbf{r}_{jk}|) / q|\mathbf{r}_{a_i} - \mathbf{r}_{jk}|, \quad \phi'_{ijk}(q) = \sin(q|\mathbf{r}_{a_i} - \mathbf{r}'_{jk}|) / q|\mathbf{r}_{a_i} - \mathbf{r}'_{jk}|, \quad (14d)$$

$$\eta_{ijk}(q) = \sin(q|\mathbf{r}_{t_i} - \mathbf{r}_{jk}|) / q|\mathbf{r}_{t_i} - \mathbf{r}_{jk}|, \quad \eta'_{ijk}(q) = \sin(q|\mathbf{r}_{t_i} - \mathbf{r}'_{jk}|) / q|\mathbf{r}_{t_i} - \mathbf{r}'_{jk}|, \quad (14e)$$

$$\gamma_{ijkl}(q) = \frac{\sin(q|\mathbf{r}_{ij} - \mathbf{r}_{kl}|)}{q|\mathbf{r}_{ij} - \mathbf{r}_{kl}|}, \quad \gamma'_{ijkl}(q) = \frac{\sin(q|\mathbf{r}_{ij} - \mathbf{r}'_{kl}|)}{q|\mathbf{r}_{ij} - \mathbf{r}'_{kl}|}, \quad \gamma''_{ijkl}(q) = \frac{\sin(q|\mathbf{r}'_{ij} - \mathbf{r}'_{kl}|)}{q|\mathbf{r}'_{ij} - \mathbf{r}'_{kl}|}. \quad (14f)$$

So the exact interstitial formation energy is the sum total of Eqs. 12 and 13 ($E_{FH}^u = E_{FH}^u + E_{fRH}^u$) and the formulation for single interstitial formation energy can be obtained by having $t=1$.⁷

VI. DIFFUSION VIA VACANCY MECHANISM

According to LeClaire,¹⁸ for vacancy controlled diffusion the differential change in the activation energy for impurity diffusion and self-diffusion is given by

and

$$\begin{aligned}
E_{fH}^u = & \sum_{q_0}^t 2[\cos(\mathbf{q}_0 \cdot \mathbf{r}_{t_i}) - 1]U(q_0) - \sum_{q_0}^t \frac{tq_0}{3} \frac{\partial U(q_0)}{\partial q_0} \\
& + \frac{\Omega_H}{2\pi^2} \int_0^\infty \sum_{i=1}^t \sum_{j=1}^t \xi_{ij}(q)U(q)q^2 dq . \quad (12)
\end{aligned}$$

As in the previous cases, the relaxation of the surrounding neighbors of an interstitial contributes much to the interstitial formation and the calculation of this part is important for close-packed structures like fcc metals. Let s be the number of relaxed neighbors around an interstitial; then the contribution of relaxation energy in t -interstitial formation is

$$\begin{aligned}
E_{fR}^u = & \sum_{q_0}^t \sum_{i=1}^s \sum_{j=1}^s 2[\cos(\mathbf{q}_0 \cdot \mathbf{r}'_{ij}) - \cos(\mathbf{q}_0 \cdot \mathbf{r}_{ij})]U(q_0) \\
& + \frac{\Omega_H}{2\pi^2} \int_0^\infty B(q)U(q)q^2 dq , \quad (13)
\end{aligned}$$

where

$$\begin{aligned}
B(q) = & 2 \sum_{i=1}^t \sum_{j=1}^t \sum_{k=1}^s [\eta'_{ijk}(q) - \eta_{ijk}(q)] \\
& + \sum_{i=1}^t \sum_{j=1}^s \sum_{k=1}^t \sum_{l=1}^s [\gamma_{ijkl}(q) - 2\gamma'_{ijkl}(q) + \gamma''_{ijkl}(q)] \quad (13a)
\end{aligned}$$

and

$$\Delta Q = \Delta E_F + \Delta E_M - C, \quad (15)$$

where ΔE_F is the difference between the energy to form a vacancy next to an impurity atom and the energy to form a vacancy in the pure solvent, ΔE_M the difference between energy for a vacancy-impurity atom exchange and the energy for a vacancy-host-atom exchange, and C the temperature-dependent correlation factor for impurity diffusion. It is possible to calculate all three terms within the framework of pseudopotential theory. By considering only monovacancy self-diffusion and impurity diffusion, these above expressions can be deduced using Eqs. (5), (7), (9), and (10) as

$$\Delta E_F = \Delta E_f + \Delta E_{fR}, \quad (16a)$$

$$\Delta E_M = \Delta E_m + \Delta E_{mR}, \quad (16b)$$

with

$$\Delta E_f = -(\Omega_H/\pi^2) \int_0^\infty \Delta U(q) [\sin(q|\mathbf{r}_v - \mathbf{r}_I|)/q|\mathbf{r}_v - \mathbf{r}_I|] q^2 dq, \quad (17a)$$

$$\Delta E_{fR} = (\Omega_H/\pi^2) \int_0^\infty \Delta U(q) \sum_{i=1}^n [\sin(q|\mathbf{r}_I - \mathbf{r}'_i|)/q|\mathbf{r}_I - \mathbf{r}'_i| - \sin(q|\mathbf{r}_I - \mathbf{r}_i|)/q|\mathbf{r}_I - \mathbf{r}_i|] q^2 dq, \quad (17b)$$

$$\Delta E_m = \sum_{q_0} 2[\cos(\mathbf{q}_0 \cdot \mathbf{r}_a) - 1] \Delta U(q_0) + \frac{\Omega_H}{\pi^2} \int_0^\infty \left[1 + \frac{\sin(q|\mathbf{r}_v - \mathbf{r}_I|)}{q|\mathbf{r}_v - \mathbf{r}_I|} - \frac{\sin(q|\mathbf{r}_I - \mathbf{r}_a|)}{q|\mathbf{r}_I - \mathbf{r}_a|} - \frac{\sin(q|\mathbf{r}_v - \mathbf{r}_a|)}{q|\mathbf{r}_v - \mathbf{r}_a|} \right] \Delta U(q) q^2 dq, \quad (17c)$$

and

$$\Delta E_{mR} = (\Omega_H/\pi^2) \int_0^\infty \Delta U(q) \sum_{i=1}^k [\sin(q|\mathbf{r}_a - \mathbf{r}'_i|)/q|\mathbf{r}_a - \mathbf{r}'_i| - \sin(q|\mathbf{r}_a - \mathbf{r}_i|)/q|\mathbf{r}_a - \mathbf{r}_i|] q^2 dq. \quad (17d)$$

Finally the temperature-dependent correlation factor^{18,19} is given by

$$C = \frac{D_2 f_0}{D_0} \exp \left[\frac{C}{RT} \right] \frac{(\Delta E_M - \Delta E_{M1}) \exp[-(\Delta E_M + \Delta E_{M1})/RT] + 7F/2(\Delta E_M - \Delta E_{M3}) \exp[-(\Delta E_M + \Delta E_{M3})/RT]}{[\exp(-\Delta E_{M1}/RT) + (7F/2) \exp(-\Delta E_{M3}/RT)]^2}, \quad (16c)$$

where $f_0 = 0.78146$, $F = 5.15/7$, D_2 and D_0 are the pre-exponential factors for impurity diffusion and self-diffusion, ΔE_{M1} the change in migration energy for vacancy-host-atom exchange, the host atom being at the near-neighbor position of the impurity, and ΔE_{M3} the change in migration for vacancy-host-atom exchange, the host atom being at the near-neighbor position of the vacancy but not at the near-neighbor position of the impurity. The expressions for these energy terms have been derived from Eqs. (9) and (10) as

$$\Delta E_{Mi} = \Delta E_{mi} + \Delta E_{mRi}, \quad (18)$$

where

$$\Delta E_{mi} = (\Omega_H/\pi^2) \int_0^\infty [\sin(q|\mathbf{r}_a - \mathbf{r}_I|)/q|\mathbf{r}_a - \mathbf{r}_I| - \sin(q|\mathbf{r}_m - \mathbf{r}_I|)/q|\mathbf{r}_m - \mathbf{r}_I|] \Delta U(q) q^2 dq \quad (18a)$$

and

$$\Delta E_{mRi} = (\Omega_H/\pi^2) \int_0^\infty \sum_{i=1}^k [\sin(q|\mathbf{r}_I - \mathbf{r}'_i|)/q|\mathbf{r}_I - \mathbf{r}'_i| - \sin(q|\mathbf{r}_I - \mathbf{r}_i|)/q|\mathbf{r}_I - \mathbf{r}_i|] \Delta U(q) q^2 dq, \quad (18b)$$

with $i = 1$ and 3 . In the above expressions, \mathbf{r}_v is the position vector for the vacancy, \mathbf{r}_m the position vector for the migrating atom, \mathbf{r}_a the activated position for the migrating atom, \mathbf{r}_I the impurity position, and \mathbf{r}'_i the relaxed position of the i th neighbor whose initial position is \mathbf{r}_i . The impurity is placed at the near-neighbor position of the vacancy. For a nonvacancy mechanism T can be taken as $0.85T_H$, T_H being the melting temperature of the host.^{19,20}

VII. RESULTS AND DISCUSSIONS

Calculations of vacancy-formation energy (E_{FH}^{1v}), migration energy (E_{MH}^{1v}), activation energy for self-diffusion (Q_0) and their differential changes (i.e., ΔE_F , ΔE_M , and ΔQ), and finally the temperature-dependent correlation factor (C) have been done in this paper for fcc metals such as copper, silver, and gold and different dilute alloy systems of them. In these calculations, the integration

over quasi-continuous wave numbers has been done by a quadrature technique and the discrete sum over lattice wave numbers has been done using the expression

$$\mathbf{q}_0 = (m_1/N_1)\mathbf{q}_1 + (m_2/N_2)\mathbf{q}_2 + (m_3/N_3)\mathbf{q}_3, \quad (19)$$

where $N_1N_2N_3=N$, the number of ions and (m_i/N_i) are positive or negative integers including zero. Three different combinations of potentials and exchange-correlation energies have been used here viz. (i) Aschroft's potential with Hubbard's function^{8,9} (denoted henceforth as AH), (ii) Aschroft's potential with Taylor's function²¹ (denoted as AT), and (iii) the local form of Heine and Abarenkov's potential⁹ with Taylor's function (denoted as HAT). The impurity potential $\omega_I(q)$ in the solvent lattice has been defined in the form

$$\omega_I(q) = [\Omega_I \epsilon_I(q) / \Omega_H \epsilon_H(q)] \omega_I^0(q), \quad (20)$$

where $\omega_I^0(q)$ is the form factor for the impurity in its pure state and Ω_I and $\epsilon_I(q)$ are the corresponding atomic volume and the dielectric function, respectively.

The input parameters of these models and the calculated values of E_{FH}^{1v} and Q_0 are shown in Table I. The relaxation energy of the surrounding neighbors during vacancy formation has been neglected for its smallness ($E_{fR}^{1v}=0$). The calculation of relaxation energy during

vacancy migration utilizes, for simplicity, only four nearest-neighbor atoms around the migrating atom at its activated configuration with $\mathbf{r}'_i = \mathbf{r}_i + \delta$, δ being the amount of relaxation. The value of δ has been fixed after minimizing the expression for the relaxation energy (E_{mR}^{1v}) using any one combination (say AT) and this same value of δ has been used for the calculation with all other combinations, since they have been tested not to change significantly with potentials and exchange forms.¹⁶ It has been found that Aschroft's model could reproduce the correct order of magnitude of E_{FH}^{1v} , while the HAT combination agrees moderately. Also it is clear from Table I that the AT combination is inadequate for Q_0 calculation, while AH and HAT combinations agree considerably, with the last one a better choice, though for aluminum no combinations reproduces correctly. More sensitive potentials are expected to produce better agreement. Also, since the calculations of these quantities involve the calculation of differences between some large numbers, careful attention has been paid in carrying out accurate numerical computations.

Further calculations of the differential activation energy (ΔQ) in dilute alloys of copper, silver, and gold have been done, using the above three combinations of potentials and exchange-correlation forms. These calculations show that the differential change in the relaxation energy

TABLE I. Input parameters and monovacancy formation and activation energy for self-diffusion.

Input parameters			Output parameters in eV					
Metal combination with parameters			δ 's in units of lattice constant		E_{FH}^{1v}		Q_0	
			$\delta_x = \delta_y$	δ_z	Calc.	Expt.	Calc.	Expt.
Cu	AH	$r_c = 0.0427 \text{ nm}^a$	0.0341	0.0682	-0.101	1.130 ^b	2.155	2.09 ^b
	AT	$r_c = 0.0427 \text{ nm}^a$			-0.079	0.980 ^c	0.241	2.15 ^c
	HAT	$r_m = 0.1274 \text{ nm}^d$ $A = 11.303 \text{ eV}$			1.488	1.280 ^e	2.389	
Ag	AH	$r_c = 0.0550 \text{ nm}^a$	0.03	0.06	-0.030	1.025 ^b	2.015	1.82 ^b
	AT	$r_c = 0.0550 \text{ nm}^a$			-0.025	1.09 ^c	0.480	1.92 ^c
	HAT	$r_m = 0.1437 \text{ nm}^d$ $A = 10.019 \text{ eV}$			1.227	1.16 ^c	2.063	
Au	AH	$r_c = 0.0429 \text{ nm}^a$	0.03	0.06	-0.354	0.900 ^b	1.607	1.75 ^b
	AT	$r_c = 0.0429 \text{ nm}^a$			-0.336	0.980 ^c	-0.061	1.81 ^c
	HAT	$r_m = 0.1437 \text{ nm}^d$ $A = 10.021 \text{ eV}$			1.241	0.97 ^c	2.072	
Al	AH	$r_c = 0.0593 \text{ nm}^a$	0.029	0.058	-0.841	0.665 ^b	2.135	1.31 ^b
	AT	$r_c = 0.0593 \text{ nm}^a$			-2.050	0.760 ^c	-2.050	1.25 ^c
	HAT	$r_m = 0.1058 \text{ nm}^f$ $A = 37.550 \text{ eV}$			3.098	0.620 ^c	2.868	
Pb	AH	$r_c = 0.0593 \text{ nm}^a$	0.0225	0.0450	-2.329	0.580 ^g	13.646	1.10 ⁱ
	AT	$r_c = 0.0593 \text{ nm}^a$			-0.177	0.50 ^g	0.257	1.13 ⁱ
	HAT	$r_m = 0.1064 \text{ nm}^h$ $A = 43.300 \text{ eV}$			0.527	0.52 ^c	2.072	1.07 ⁱ

^aReference 9.

^bReferences 24 and 25.

^cReference 26.

^dReference 23.

^eReference 27.

^fReference 1.

^gReference 13.

^hReference 15.

ⁱReference 6.

during vacancy formation (ΔE_{fR}) is very small in both homovalent and heterovalent systems ($\Delta E_{fR}=0$) and so this is neglected in these calculations. Calculations of ΔE_f , ΔE_m and ΔE_{mR} have also been done and are shown in Table II together with C and ΔQ . The temperature-dependent correlation factor (C) has been determined from Eq. (16c) in which ΔE_{M1} and ΔE_{M3} are defined in Eqs. (18) and the experimental values of D_2 and D_0 have been used. These calculations show that the absolute value of C is small in homovalent systems in comparison to those in heterovalent systems. The absolute value of $\Delta E_f/(\Delta E_m + \Delta E_{mR})$ lies between 0.15 and 0.23, which is in fair agreement with the empirically predicted value of 0.17 of the above quantity by Neumann.^{19,20} The values of ΔE_{M1} and ΔE_{M3} are also in agreement with the empirically predicted value of Neumann ($\Delta E_{M1}=0.19\Delta E_M$ and $\Delta E_{M3}=-0.16\Delta E_M$).²⁰

Though these calculations show fair agreement with experiments, this method is still not above criticism. First, it must be kept in mind that although our formula-

tions are generalized, the calculation of the activation energy considers only monovacancy self-diffusion and impurity diffusion. So the deviation from the experimental values of these calculated values of ΔQ might be due to the presence of other diffusion mechanisms. Second, calculation indicates that the relaxation energy at the saddle-point configuration plays a significant role in ΔQ calculation. In fact, the contribution of ΔE_{mR} is about 40% of the total migration energy (ΔE_M). Also to a first approximation, only the relaxation of the first four nearest neighbors around the activated position has been taken into account, which cannot be accurate. In the saddle point, the atom and the vacancy will have a relaxation volume of about 0.2 atomic volume, which will not be concentrated on to the next neighbors. Third, the calculation of C according to Eq. (16c) uses the semi-empirical form of LeClaire¹⁸ and Neumann and co-workers.^{19,20} Fourth, it is clearly understood that Heine and Abarenkov's model reproduces the experimental values of defect parameters more correctly than

TABLE II. Calculated and experimental defect energy parameters.

System	Combination	All energies in eV					
		ΔE_F	ΔE_M	C	ΔQ	Q_2^a (expt.)	ΔQ^a (expt.)
Cu-Ag	AH	-0.0056	0.0815	0.2286	-0.1527	2.0165	-0.0736
	AT	0.0301	0.0139	0.3850	-0.3411		-0.1335
	HAT	-0.0524	-0.2219	-0.1951	-0.0792		
Cu-Au	AH	0	0	0	0	1.9818	-0.1082
	AT	0	0	0	0		-0.1682
	HAT	-0.0522	-0.2215	-0.1094	-0.1643		
Cu-Zn	AH	0.0789	-1.6020	-1.3145	-0.2086	1.9775	-0.1125
	AT	-0.0042	0.0252	0.4035	0.3827	2.06	-0.1725
	HAT	-0.0339	-0.1759	-0.1169	-0.0929		-0.09
Cu-Sn	AH	0.2627	-4.7628	-3.7670	-0.7332	1.9514	-0.1386
	AT	-0.0188	0.3746	0.6788	0.3230		-0.1986
	HAT	-0.2878	-1.0805	-0.7890	-0.5793		
Ag-Cu	AH	0.0029	-0.0595	-0.0241	-0.0325	1.9991	0.1792
	AT	-0.0040	-0.0099	-0.0029	-0.0110		0.0791
	HAT	0.0314	0.1424	0.0079	0.1660		
Ag-Au	AH	0.0029	-0.0595	-0.0178	-0.0388	1.973	0.153
	AT	-0.0040	-0.0099	-0.0020	-0.0118	2.09	0.053
	HAT	0.0001	0.0003	0.0001	0.0003		
Ag-Zn	AH	0.1023	-1.4430	-0.1169	-0.0929	1.8084	-0.0116
	AT	0.0131	0.0929	-1.0967	-0.2501		-0.1116
	HAT	0.0303	0.1578	0.4286	-0.3341		
Ag-Sn	AH	0.3147	-4.0109	-3.1019	-0.5943	1.7043	-0.1158
	AT	0.0354	0.6856	1.0609	-0.3400		-0.2157
	HAT	-0.0815	0.0495	0.5261	-0.5581		
Au-Cu	AH	0	0	0	0	1.7628	0.0128
	AT	0	0	0	0		
	HAT	0.0318	0.1438	0.0186	0.157		
Au-Ag	AH	0.0022	0.1049	0.1464	-0.0393	1.7433	-0.0067
	AT	0.0094	0.0600	-0.1652	-0.0958	1.9991	
	HAT	-0.0001	-0.0003	0.0003	-0.0001		
Au-Zn	AH	0.1200	-1.2898	-0.9597	-0.2102		
	AT	0.0324	0.2601	0.5657	-0.2732		
	HAT	0.0301	0.1555	0.4873	-0.3018		
Au-Sn	AT	0.3541	-3.8131	-3.0507	-0.4083	1.4831	-0.2669
	AT	0.0648	1.0077	1.3133	-0.2408		-0.3269
	HAT	-0.0849	0.0593	0.4088	-0.4344		

^aReferences 28 and 29.

Aschroft's one-parameter model. But both of these models are simple potentials. There are also questions about the validity of second-order perturbation technique in Harrison's approach.²² So considering all these limitations, a more sophisticated multiparameter model like Dagens¹¹ or Heine and Abarenkov's model with approximate overall explanation of all atomic properties is perhaps a better choice and the agreement of ΔQ with the experimental values will be more satisfactory.

VIII. CONCLUSIONS

Although there are some previous attempts for vacancy formation- and migration-energy calculations in fcc

metals using pseudopotential formalism, the effect of impurities has been introduced in the present formulation in a generalized way and has been applied to several cases of impurity diffusion. It seems that a proper choice of a pseudopotential is very important for such calculations and careful attention must be paid in achieving accuracy in numerical computation in order to arrive at a meaningful result. However, the calculation also points out that the effect of relaxation during migration must be taken into account for any theoretical consideration of self-diffusion and impurity diffusion phenomena.

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